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# INSENSITIVE HIGH ENERGY PROPELLANTS FOR ADVANCED GUN CONCEPTS

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Substantial improvements in the performance of solid propellant guns have resulted from the development of higher energy propellants, higher loading density charge concepts, and highly progressive propellant geometries required to utilize efficiently resulting increases in total energy. Unfortunately, these same features typically lead to increases in ammunition vulnerability to enemy threats. This paper describes the development of a new approach in the U.S. Army to address propellant energy and sensitivity from the very beginning of the development cycle as a single set of critical design requirements.

## BACKGROUND – THE QUEST FOR HIGHER PERFORMANCE

The quest for higher interior ballistic performance for any gun system ultimately comes down to two challenges: more energy in the propelling charge, and its efficient transfer to the projectile. For conventional guns, this means propellant formulations with higher specific energies, charge configurations that increase overall charge loading density (which for advanced kinetic energy rounds with long rod penetrators extending well back into the charge may be problematic), and techniques for programming energy release such that the maximum desirable system pressure is reached as early as possible, and nearly maintained as long as possible, preferably right until the moment of propellant burnout.

Complete success in these challenges would lead to a flat pressure-travel curve with projectile base pressure at the maximum level for a duration allowable by overall system constraints. Today's high performance tank guns are already extremely well designed. While piezometric efficiencies (the ratio of mean pressure to peak breech pressure) are on the order of 50% and thermodynamic efficiencies (the ratio of projectile muzzle kinetic energy [MKE] to available chemical energy of the propellant) only 25%, values for the more recent ballistic ratio (defined here as the ratio of the actual MKE to that obtainable if the same total charge were burned at constant pressure) approach or even exceed 90%! Clearly, the charge design community has done an excellent job in extracting performance from a given energy source, the obvious inference being that focus should be

placed on increasing the energy in the system – but without any reduction in the efficiency of its use.

For the past century, virtually all of the world's production gun propellants have been based on the use of nitrocellulose (NC), with NC-base and the higher energy doublebase propellants (also with nitroglycerine or related energetic plasticizers) most used. However, development efforts over the past few decades have addressed the use of new materials that raise energy density without unacceptable increases in flame temperature. Much work addressed the use of the crystalline, cyclic nitramines RDX and HMX, and by the 1980's, joint efforts by the U.S. Navy and Army led to the first service-qualified nitramine-based gun propellant for low-vulnerability (LOVA) ammunition [1]. Since then, alternative high energy density ingredients such as CL20 [2], TNAZ (3,3-trinitroazetidine), and ADN (ammonium dinitramide) have been identified and evaluated in possible new advanced gun propellants. CL20 is highly attractive as an energetic filler because of its heat of formation (+100 kcal/mole), density (2.04 g/cc), and impact on burning rates.

Concurrently, new binders were developed to replace the historical workhorse NC. Thermoplastic elastomers (TPEs) process like thermoplastics but behave like elastomers at gun operating temperatures, while offering the opportunity for ready inclusion of energetic fillers, good physical properties, and reprocessibility. Early LOVA formulations were based on energetic fillers in nonenergetic binders, but the quest for higher performance led to a concentration on the use of energetic TPEs (or ETPEs, such as the oxetanes BAMO [3,3-Bis (azidomethyl) oxetane] and AMMO [3-Azido-3-methyloxetane]) [3].

However, increased available propellant energy is useful only if its release can be controlled. Perforated cylindrical grains have long been used to provide progressively increasing burning surfaces. Stick propellants pack better, but gas production within long perforations can lead to overpressurization and fracture – previously limiting propellant designers to the use of single-perforated sticks with longitudinal slots; however, the recent use of partial transverse cuts controls fracture and enables use of multiperforated sticks [4]. Current approaches decouple gas production rates before and after peak pressure in the gun. Two such concepts include programmed-splitting geometries [5], which effect a rapid and large change in area, and layered propellants [6], made practical by the use of TPE propellants by allowing use of adjacent layers of materials with different burning rates yet adequate chemical stability. Layered propellants also increase loading densities by 40%.

## INTRODUCTION OF THE IHEM PROGRAM

Current research in gun propulsion in the United States is driven by requirements for future, lightweight combat vehicles, with missions including both direct and indirect fire. Needed improvements in system lethality and survivability translate, for propellants, into more energy and less sensitivity. Hence, the U.S. Army Research Laboratory (ARL) restructured its energetic materials program, combining major portions of its propellants and survivability programs into a new thrust, Insensitive High Energy Munitions (IHEM), treating these two features as coupled requirements, even at the earliest phases of research.

The program focuses on several families of new insensitive high-energy propellants (IHEPs). The first is based on current research propellants employing energetic fillers such as RDX or CL20 in ETPE oxetane binders. Such propellants have been shown to provide the substantial, required increases in specific impetus (> 1300 J/g), chemical stability, and range in burning rates needed to facilitate the use of layered propellants. They can also be configured to offer very high loading densities (>1.4 g/cm$^3$). Plasma ignition, however, is required for acceptable ignition [7] and accompanying high performance [8] of charges so assembled. A primary remaining challenge for such formulations is to modify chemistry and physical product so as to achieve required reductions in sensitivity/vulnerablity.

This challenge is being addressed through use of a family of new screening devices capable of evaluating performance, sensitivity, and erosivity with the smallest possible quantities of often expensive (at the research stage) candidate materials. “Smart testing” of carefully selected and manufactured samples evaluating the roles of formulation, particle sizes, additives, and processing is then coupled with extensive modeling efforts to assess a wide range of variables and arrive at the desired propellant characteristics.

Only brief mention is made here of a number of recent experimental techniques specifically developed to support the testing of new candidate formulations when cost or scarcity necessitates use of very small quantities of material; we refer you to the references for more detail. First is the 25-cm$^3$ micro-closed bomb (rather than the usual 200 cm$^3$), allowing burning rate determinations at normal loading densities with <10 g of propellant. Comparability of results with conventional test fixtures has been demonstrated [9]. Evaluation of ballistic parameters with small quantities of available materials presents a significant challenge. To that end, ARL has developed a suite of medium-caliber diagnostic devices, capable of exposing relatively small quantities (30 grams to 200 grams) of novel propellant formulations to the interior ballistic environment such that the propellant’s temperature sensitivity, material integrity, and ease of ignition and flamespreading properties are revealed. These fixtures include a 30-mm gun and a short gun/interrupted burner [10]. In addition, an existing erosivity measurement fixture was recently refurbished and is being used to provide a relative ranking of gun propellant erosivities, with attention to the influence of chemistry as well as flame temperature [11].

## RECENT APPROACHES TO VULNERABILITY SCREENING

Propulsion charge vulnerability is a function of design and propellant geometry, but for new IHEP formulations, parameters that influence vulnerability must be identified in small-scale tests. Ballistic impacts on propulsion charges lead to thermal and mechanical ignition stimuli. The latter is divided into shock and nonshock stimuli and is emphasized here. Upon impact, propellant response is either nondetonative or detonative combustion; either can be catastrophic. Three important sensitivity parameters are shock sensitivity, nonshock sensitivity, and mechanical properties. One mechanical property that correlates with response is failure modulus (negative slope of stress-strain curve after material failure) [12], measured in a servohydraulic tester at various temperatures [13] and shifted to high strain rates using time-temperature superposition [14]. Brittle propellants have large failure moduli and tend to higher responses than propellants that work harden.

ARL uses two experiments to evaluate nonshock sensitivity. One is the ballistic impact chamber (BIC) [15], a drop-weight machine using a 30–50 mg sample in a semi-closed volume. Pressure upon impact is recorded; the pressure-time integral indicates sample energy, and the initial pressure rise in the few microseconds after ignition indicates reaction strength [15]. Both relate to vulnerability, though the exact relationship is clouded by factors such as mechanical properties. The second nonshock test is a shear-punch test. With a modified split-Hopkinson pressure bar that punches a core from a sample (Figure 1a). Duration, shear rate, and pressure on the shear plane can be independently varied. The measured reflected and transmitted strains in the bars permit evaluation of properties on the shear plane. Samples sheared at rates below the reaction threshold can be analyzed with scanning-electron-microscopy to provide insight into the shear process.

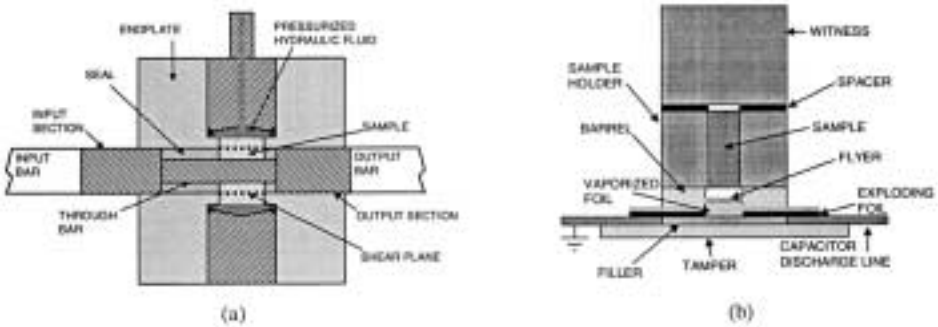


Figure 1. (a) Modified Spilt-Hopkinson pressure bar for measurement of shear sensitivity, and (b) electric flyer plate test apparatus to measure high-pressure shock sensitivity.

Two shock regimes are relevant to vulnerability: a low-pressure, long-duration regime, determining the minimum stimulus to detonate a charge, and a high-pressure short-duration regime, influencing detonation propagation between grains. High-pressure sensitivity relates to critical propellant dimensions for detonation. If a grain is sufficiently insensitive to high-pressure, short-duration shocks, full charge detonation should be preventable even if material in the impact area detonates. ARL is evaluating high-pressure shock sensitivity using an electric-flyer shock test (Figure 1b). A high-voltage capacitor is discharged across a thin metal foil, which is vaporized by ohmic heating and propels a thin flyer plate into a 150–200 mg sample at up to 5 mm/μs. Flyer thickness, material, and discharge voltage are varied to change the incident shock. We plan to overdrive detonation in samples smaller than detonation failure dimensions to examine detonation failure.

Mechanical properties, BIC, shear-punch, and electric-flyer tests offer a suite of small-scale vulnerability screening tools for advanced propulsion charges. The measured properties provide insight to propellant developers designed new formulations and system developers designing high-performance, reduced-vulnerability charges.

## THE SEARCH FOR ADVANCED IHEM/IHEP CONCEPTS

Longer term efforts address the development of advanced IHEPs, including the use of new highly energetic molecules, nanomaterials for improved combustion efficiency and higher burning rates, and new composite matrixes for improved mechanical properties. Materials difficult to ignite or initiate except by specific stimuli are particularly sought.

Opportunities for new IHEPs are being addressed via a multidisciplinary approach involving predictive modeling/simulation and complementary laboratory experimentation. Theoretical chemistry is used for further understanding of the mechanisms that control both energy and sensitivity. Such information can be used to design new energetic materials with specific properties, including initiation specificity, burning rate/energy release, flame temperature, mechanical/rheological properties, sensitivity, and erosivity. The computational tools described are based on quantum mechanical (QM) calculations and describe relationships between the quantum mechanical properties of an isolated molecule with its behavior on the macroscale. The predictive methods all use QM predictions of the electrostatic potential that surrounds an isolated molecule.

The first computational tool developed is used to predict Heats of Formation for gas, liquid and solid energetic materials [16], allowing assessment of detonation properties and idealized performance. Predicted Heats of Formation in the solid state (Figure 2a) have a root mean square (rms) deviation of 9.0 kcal/mol for 44 energetic materials.

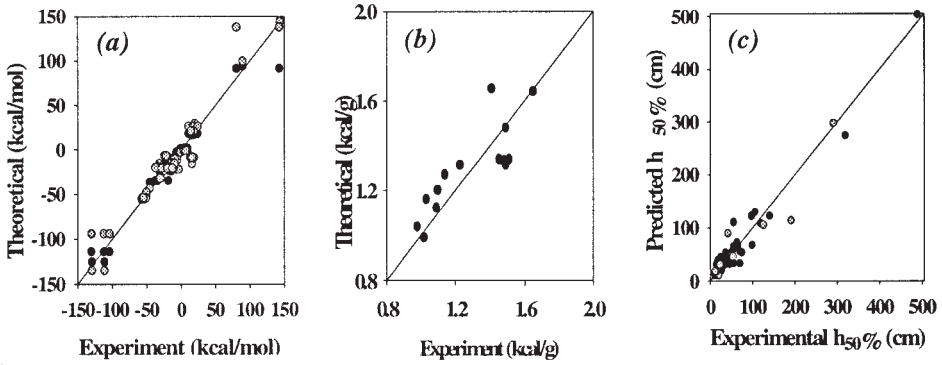


Figure 2. (a) Solid phase Heats of Formation for explosives contained in Cheetah 2.0 reactant library [17] (filled circles) and predicted using the QM methods described herein (hollow circles) vs experimental values [16]. (b) Predicted vs experimental Heats of Detonation. (c) Predicted vs experimental $h_{50\%}$ values for explosives. Solid circles denote 34 explosives with values measured by Wilson et al. [20]; hollow circles denote 11 molecules to assess predictive quality of the model. Solid line denotes exact agreement.

The Heats of Formation predicted by these methods can be ured to predict Heats of Detonation of pure and explosive formulations [18] assuming the Kamlet-Jacobs scheme to calculate detonation properties [19] (Figure 2b). Our predicted Heats of Detonation using this method were compared with predictions using the thermochemical code Cheetah 2.0. For pure explosives, the QM based results have a rms deviation from experiment of 0.138 kcal/g, whereas the Cheetah predictions have a rms deviation from experiment of

0.133 kcal/g. For explosive formulations, the QM predictions are in reasonable agreement with experimental values, with a rms deviation of 0.058 kcal/g. Although Cheetah calculations have a stronger theoretical basis for prediction of detonation properties, this methodology has the advantage that neither Heats of Formation nor densities need to be measured or estimated to calculate the Heat of Detonation of an explosive.

Finally, we address efforts to establish functional relationships between statistical properties of the electrostatic potentials for a set of energetic molecules and their impact sensitivities. Impact sensitivities may be characterized by drop-weight impact tests in terms of $h_{50\%}$, the height at which the specimen reacts 50% of the time. We performed QM calculations on 34 polynitroaromatic and benzofuroxan molecules which have undergone such measurements [20] and established a functional relationship between their $h_{50\%}$ values and properties of the electrostatic potentials. Predicted values are in good agreement with experimental values for materials ranging from the highly sensitive hexanitrobenzene to the highly insensitive explosive TATB. Impact sensitivities for 11 additional energetic molecules were then calculated and compared to experiment to determine the predictive capability of the computational tool. These molecules, not used in establishing the correlation, included PETN, RDX, HMX, β- and ε-CL-20, HNS, methyl picrate, styphnic acid, NTO, NQ and FOX-7. Figure 2c shows excellent agreement between the predicted and measured values, with a rms deviation of 22 cm from experiment.

In addition to the use of new modeling tools, new approaches to modify existing materials will expedite propellant research and development. Nanomaterials, particularly nanocomposites [22], are being investigated to achieve improved mechanical properties, ballistics, and vulnerability responses. Nanocomposites are primarily inorganic silicates containing naturally occurring sodium and potassium ions that are exchanged for organic cations with a high affinity for the host polymer. This interaction serves as the basis for the two-dimensional dispersion of modified silicates and enables much greater properties modification at low levels than with micro-scale unidirectional fibers having inherently lower surface-to-volume ratios. Typically, only a 2–5% level has been required to improve material characteristics of commercial polymers. For composite propellants containing >50% crystalline solids, a nominal 1% incorporation may be sufficient. Increased modulus and diffusion resistance, achieved in commercial nano-polymer systems, will be important for structural integrity of ETPE propellants over the wide operating temperature range.

Nanotechnology is also being pursued to tailor ETPE-based propellants for plasma ignition and burning rate modification to improve performance and vulnerability response. Chemical species that promote plasma initiation and burning rate modification (e.g., via chromophoric linkages) will be targeted as candidates for nanocomposite modification of propellants, with the goal of rendering them sensitive to plasma output, while reducing responsiveness to other sources. Analogous modification for laser-specific initiation is also feasible. Improved vulnerability response for advanced propellant configurations is intrinsically coupled to the decomposition of the energetic crystals that comprise up to 80% of these formulations. A basic understanding of shock, impact, mechanical properties and thermal sensitivity is being pursued through modeling and carefully designed small-scale experiments addressing changes in propellant crystal morphology and chernistry in response to initiation stimuli. Research is being pursued to exploit recent advances in nano-

scale characterization (e.g., high resolution imaging and chemical analysis) to help understand the very earliest processes that occur in response to initiation stimuli. Such an understanding will lead to the development of design rules and will be used to validate and refine molecular models relating vulnerability to disruption of the crystalline structure.

Advanced, although currently notional, applications of nanomaterials include the high reactivity of fuel-oxidizers in nano-scale materials, where intimate contact of fuel and oxidizer promises extremely high heat-release rates and combustion effficiency. The unique geometry of nanotube and fullerene structures offer further potential for confining energetic crystals in a nano-matrix, with unprecedented reactivity and stability – usually diametrically opposed properties. Strained ring compounds, including all-nitrogen species, offer potential for high-energy storage within intramolecular bonds. Moreover, derivitization of these compounds with energetic functional groups would further improve performance. The potential for engineering nano-modified energetic materials is vast, and realization of that potential is facilitated by recent advances in nano-scale synthesis and characterization, molecular dynamics simulations, and well-designed small-scale testing for elucidating fundamental performance and vulnerability mechanisms.

## OUTLOOK: IHEMS AND 21st CENTURY WEAPON SYSTEMS

We have reported on a program which addresses the need for IHEPs in terms of various levels of new technology. Both performance and sensitivity attributes are considered right from the earliest stages of research. In all cases, advanced modeling techniques lead the way; smart, selective testing on small quantities of new materials follows; scale up and ballistic testing are pursued only for highly attractive candidates. Primary efforts to render RDX- and CL20-filled ETPE propellants system acceptable are being complemented by longer term research endeavors addressing totally new approaches to even higher energy levels with acceptable system survivability characteristics. Such efforts, in concert with related efforts across the national and international energetic materials community, are designed to provide the revolutionary advances likely required by lightweight, highly mobile weapon systems of the 21st century.

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